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ABSTRACT

We have used Coherent Bragg Rod Analysis (COBRA) to investigate the atomic structure of a 5.6 nm thick Gd_2O_3 film epitaxially grown on a (100) GaAs substrate. COBRA is a method to directly obtain the structure of systems periodic in two-dimensions by determining the complex scattering factors along the substrate Bragg rods. The system electron density and atomic structure are obtained by Fourier transforming the complex scattering factors into real space. The results show that the stacking order of the first seven Gd_2O_3 film layers resembles the stacking order of Ga and As layers in GaAs then changes to the stacking order of cubic bulk Gd_2O_3. This behavior is distinctly different from the measured stacking order in a 2.7 nm thick Gd_2O_3 in which the GaAs stacking order persists throughout the entire film.

INTRODUCTION

When prepared as epitaxially grown thin films, the electronic properties of materials can differ significantly from their bulk properties impacting their utilization in devices. We recently developed a new technique, named COBRA [1], that involves analysis of the coherent interference of x-rays along substrate Bragg rods to provide a 3D mapping, with atomic precision, of the structure of epitaxial films and their interfaces. We applied this technique to map the electron density of a 2.7 nm thick Gd_2O_3 film on a GaAs substrate [2,3]. Our measurements showed that the Gd positions in the first few film layers were displaced so as to exactly match the positions of the underlying Ga and As. Moreover, we discovered that the stacking order of the Gd_2O_3 ,throughout the entire film, was the same as the stacking order of bulk GaAs rather than bulk Gd_2O_3. In this publication, we present results on a thicker, 5.6 nm epitaxially grown Gd_2O_3 film. This 5.6 nm film was prepared using a higher growth rate than the

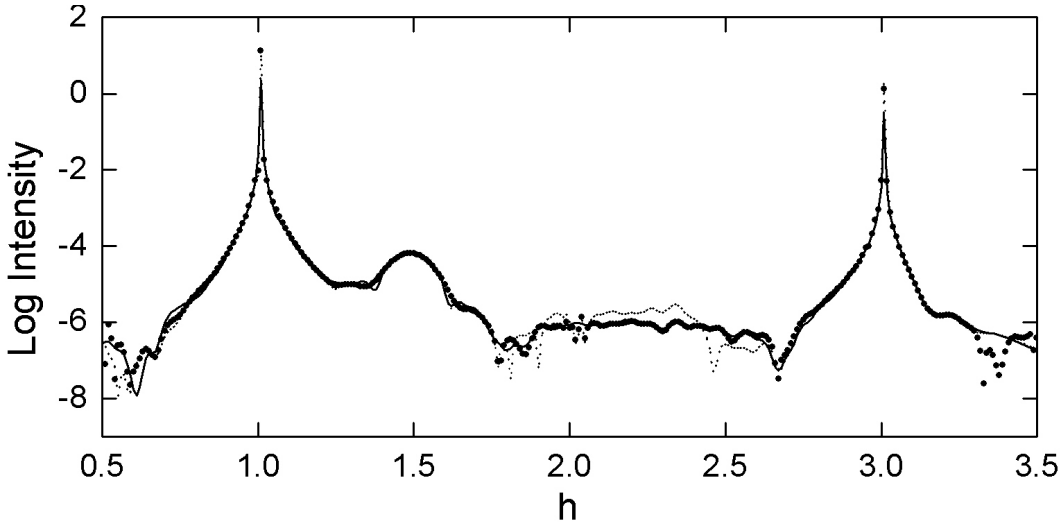

Figure 1. Log Intensity along the [h 1 -1] Bragg rod. h is given in reciprocal lattice units: dots-data; solid line-COBRA calculated intensity; dotted line-data with artificially added noise.

2.7 nm film and, although it exhibited more crystalline disorder than the thinner film, the crystalline order was of sufficiently high quality that the stacking order of the epilayers could be unambiguously determined. The stacking order measured in the 5.6 nm film, as described below, differed from the stacking order measured in the 2.7 nm film confirming both the power of COBRA for determining the fine details of structural ordering as well as the richness of possibilities for structural ordering in epitaxial films.

EXPERIMENTAL RESULTS

In order to determine the 3D electron density map of the epitaxial film, we measured the x-ray intensity along a complete set of symmetry inequivalent Bragg rods. The normalized diffraction intensities along the [h 1 -1] Bragg rod are shown in figure 1. The large peaks correspond to [1 1 -1] and [3 1 -1] Bragg peaks. The broad peak at approximately [1.5 1 -1] and the overtones are due to the Gd_2O_3 film. The diffraction intensities along the [h -1 1] Bragg rod were found to be equal to within the experimental accuracy to those on [h 1 -1] while those on [h 1 1], were completely different. These results confirm the conclusion of Kortan et al. [4] that Gd_2O_3 grows on GaAs as a single crystal with a single domain having 180^o rotational symmetry but not 90^o rotational symmetry.

The 10 keV incident beam allowed us to measure all the Bragg rods within the range $| k | \leq 3$, $| l | \leq 3$, and $0.1 < | h | \leq 3.5$ (along the [h 0 0] rod, h extended to 4.2). The diffraction intensities along rods with k+l odd were too small to be measured. So the total number of symmetry inequivalent rods measured was 13. The [h 1 -1] and [h 0 0] Bragg rod scans displayed clearly identifiable Gd_2O_3 contributions. The other Bragg rods also have intensity contributions from the Gd_2O_3 : GaAs interference, but they are much weaker.

We have analyzed the data following the COBRA procedure discussed by Sowwan et al. [3]. The first step is to choose a known structure that is similar to the structure of the system under investigation. We began by constructing a simple model of the system consisting of the semi-infinite GaAs crystal and a cubic single domain Gd_2O_3 film on top of it. The model contained the features found by Kortan et al. [4]; namely, that the Gd_2O_3 <110> axis is perpendicular to the

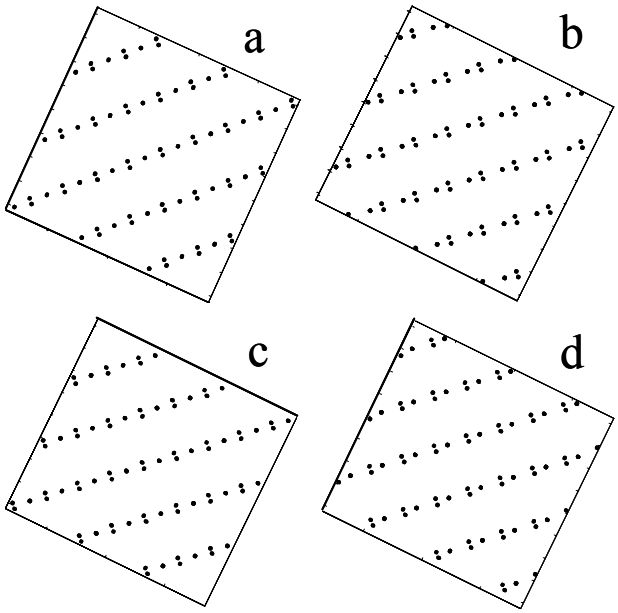

Figure 2. Gd atomic positions in 4 consecutive layers of bulk Gd_2O_3. Each panel represents 3x3 GaAs 2-D unit cells. Each dot shows the in-plane position of 4 folded Gd atoms and each dot in a pair similarly represents 2 atoms. Notice that the stacking sequence is such that in (a) there is a ridge along the diagonal, in (b) a valley; in (c) a ridge, and in (d) a valley.

(100) GaAs substrate, the <001> Gd_2O_3 axis coinciding with the <011> GaAs axis and the orthogonal <1-10> Gd_2O_3 axis coinciding with the <0-11> GaAs axis. The model further assumes in accordance with the results of Kortan et al. that three Gd_2O_3 unit cell edges match four GaAs unit cell face diagonals and one Gd_2O_3 face diagonal matches 2 GaAs face diagonals. The Gd and O atoms lie approximately in layers parallel to the interface, each layer containing both Gd and O atoms. The largest vertical distance between Gd atoms within one layer is 0.457Å as compared to the 1.92Å interlayer separation in bulk Gd_2O_3. Four such layers contain all the atoms of one unit cell. We shall concentrate our discussion mainly on the Gd atoms, which dominate the scattering.

Using the model as the reference structure and the experimentally measured diffraction intensities along the Bragg rods we calculated the real and imaginary parts of the Complex Scattering Factors (CSFs) along all 13 Bragg rods. Then using the symmetry properties of the system we calculated the CSFs along all 49 Bragg rods contained in the volume $-4.5 < h < 4.5$; $-3.5 < k < 3.5$ and $-3.5 < l < 3.5$. Finally we Fourier transformed the CSFs into real space. If the experimental results and the COBRA method were ideal the function obtained would be proportional to the system 3D electron density.

Since the experiments and the analysis are not ideal, the function obtained may have negative parts and may be non zero outside the film. We therefore zero out the negative parts and the parts that are non-zero outside the film. The resulting function may now qualify as a 3D electron density. We now test its agreement with experiment by calculating the diffraction intensity we expect to obtain from it and compare it to the experimental data. The calculated diffraction intensity is shown in figure 1 by the solid line. As seen, the calculated and experimental results are in very good agreement with each other. This quality of agreement is seen in all 13 Bragg rods.

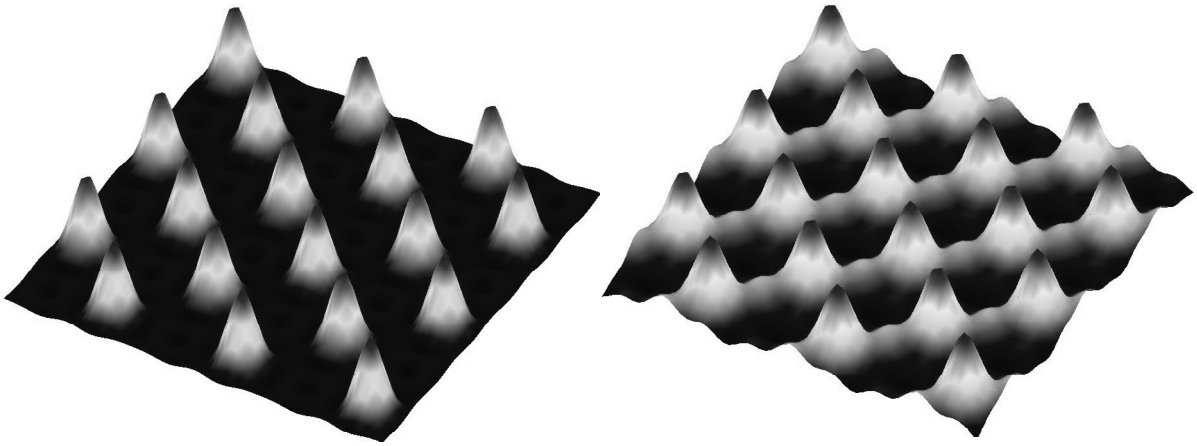

Figure 3. Electron density maps in the sixth GaAs layer below the interface (left) and the seventh Gd_2O_3 layer above the interface (right). Each panel represents 3x3 GaAs 2-D unit cells.

The fact that the 2D periodicities of the film and substrate are different means that the electron density obtained by COBRA is that of a folded structure. The folded structure is obtained by translating all the atoms parallel to the surface, using the substrate defined 2D unit cell vectors, into one substrate defined 2D unit cell. The folded positions of 4 consecutive bulk Gd layers are shown in figure 2. Each panel represents 3x3 2D GaAs unit cells. Notice that the folded positions form lines that run parallel to the square diagonal. The positions appear as single dots and pairs of dots. Each single dot represents 4 Gd atoms occupying the same in-plane position but different vertical positions and similarly each dot of a pair represents 2 Gd atoms. Notice that in 'a' we have a ridge on the main diagonal followed by a valley in 'b', a ridge in 'c', and a valley in 'd'. This defines the stacking order in bulk Gd_2O_3.

In figure 3 we display two examples of the COBRA calculated electron density maps: the sixth layer below the interface, on the substrate side, simply shows the Ga or As atoms. In the seventh layer above the interface, we see the ridge-valley Gd_2O_3 structure as expected. As in the 2.7 nm sample the small peaks correspond to groups of 4 atoms while the large ones correspond to pairs of groups of 4 atoms that have moved closer together. It turns out that further away from the interface the disorder grows much more than in the 2.7 nm sample and we cannot reliably follow the individual peaks along the ridges. However we can still follow the ridges and valleys.

In figure 4 we display the difference between the average electron density along the main diagonal minus the average along the parallel line next to it. So if the ridge is along the main diagonal, the valley will be along the line next to it and the difference is positive. In contrast if the valley is along the main diagonal the ridge is along the line next to it and the difference is negative. In the region marked 'A' we see 8 positive and negative peaks that correspond to the top 8 GaAs layers. In this region the contrast between ridges and valleys is large, meaning that the system is highly ordered. The disorder increases as we progress into the film. Region ‘B’ is the transition region between GaAs and Gd_2O_3. The Gd_2O_3 layers begin in region ‘C’ and continue into region ‘D’. Notice that the differences have two positive and two negative peaks. This means that the stacking order is such that along the main diagonal we have a ridge followed by a ridge followed by two valleys. This sequence is the same as in GaAs but different from the sequence in bulk Gd_2O_3. The GaAs stacking sequence persists into region ‘C’, then, in region ‘D’, the stacking order becomes ridge, valley, ridge, valley etc., namely the stacking order becomes the same as in bulk Gd_2O_3. This can also be clearly seen in the electron density maps

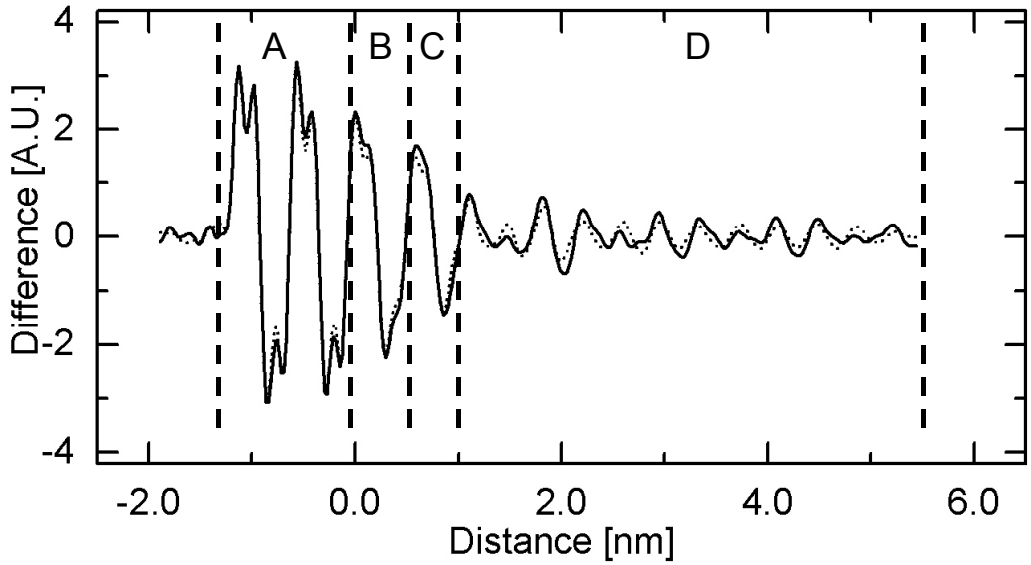

Figure 4. The difference between the average electron density along the main diagonal and along the line next to it as a function of the distance from the nominal interface: solid line-calculated from measured data, dotted line-calculated from data with artificially added noise. A positive peak is a ridge along the diagonal and a minimum is a valley along the diagonal.

shown in figure 5.This result is different from that in the 2.7 nm film. There the stacking order of the GaAs persisted throughout the entire thickness of the film.

In any experiment it is important to check the reliability of the results and conclusions in view of the fact that the experiments and data analysis are not ideal. To partially address this issue we have used an approach that has been effectively applied to the analysis of XAFS spectra [5]. Our previous experience is that the COBRA procedure usually converges rapidly toward a well-defined structure after a few iterations. We proceed on the assumption that this convergence is unique. Then we use the difference between the calculated and measured diffraction intensities to calculate an artificial noise function (ANF). We generate a stochastic phase factor and limit its spectral range to the spectral range of the data. The ANF is obtained by multiplying the difference between the calculated and experimental intensities by the real part of the phase factor. This ANF is added to the data and the resultant is treated as new data and analyzed using COBRA. Only those results and conclusions that are consistent with the original data and with data containing the ANF are deemed reliable and valid. An example of the data with ANF is shown in figure 1 and the corresponding difference between the average electron density along the main diagonal and the line next to it is shown in figure 4. As seen, the two curves, one calculated from the original data and the second calculated from the data with ANF, are in good agreement in all the regions. This supports the validity of our results and conclusions.

CONCLUSIONS

The results of this study show that in the 5.6 nm thick film, the first 7 Gd_2O_3 layers have the stacking order of GaAs. This is similar to the results found in the 2.7 nm film except that in the thinner film this stacking order persisted throughout the entire film thickness. The in-plane

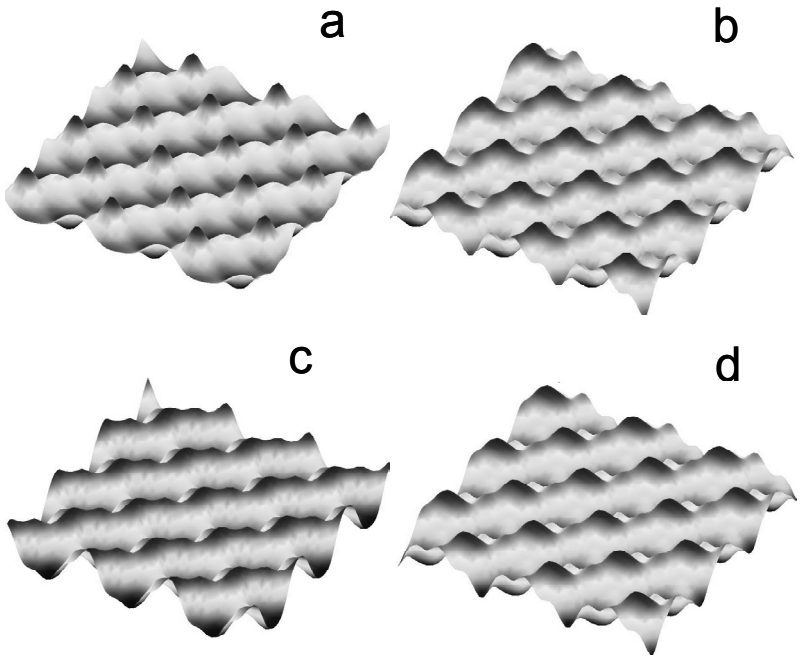

Figure 5. The electron density maps on 4 consecutive Gd_2O_3 layers in region D. Each panel represents 3x3 GaAs 2-D unit cells. Notice that the stacking sequence is ridge, valley, ridge, valley along the diagonal, the same as in bulk Gd_2O_3

displacement of the Gd atoms towards the in-plane positions of the Ga and As is also observed here. However starting from the 8th layer and above the stacking order is that of bulk Gd_2O_3. The fact that the Gd_2O_3 film structure is well adapted to the GaAs structure close to the interface suggests that this film will have good passivation properties as confirmed for thinner films [6].

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